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ELEMENTAL COMPOSITION OF COAL FLY ASH:  
MATLA COAL POWER STATION IN THE MPUMALANGA  
PROVINCE IN SOUTH AFRICA CASE STUDY USING  
NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

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Элементный состав золы от сжигания угля на тепловой электростанции в Мальте, провинция Мпумаланга Южной Африки, определенный с помощью ядерно-физических аналитических методов

Эпитепловой нейтронный активационный анализ наряду с ИСП-АОЭ, ИСП-МС с лазерной абляцией и РФА использовали для определения элементного содержания в золе, образующейся при сжигании угля на тепловой электростанции в Мальте, провинция Мпумаланга Южной Африки. В общей сложности с помощью четырех аналитических методов были определены 54 макро-, микро- и редкоземельных элемента. Было проведено сравнение результатов анализа, обсуждены расхождения, и продемонстрированы преимущества и недостатки каждого из методов. Было показано, что концентрация элементов в данной конкретной золе имеет тот же порядок величин, что и стандарт Coal Fly Ash 1633b NIST.

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Eze Ch.P. et al.

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Elemental Composition of Coal Fly Ash:  
Matla Coal Power Station in the Mpumalanga Province in South Africa  
Case Study Using Nuclear and Related Analytical Techniques

Epithermal neutron activation analysis along with ICP-OES, LA ICP-MS, and XRF were used to determine the elemental composition of coal fly ash from the Malta coal power station in the Mpumalanga province of South Africa. A total of 54 major, trace and rare-earth elements were obtained by the four analytical techniques. The results were compared and the discrepancies discussed to show the merits and drawbacks of each of the techniques. It was shown that the elemental content of this particular coal fly ash are of the same order as the NIST standard reference material Coal Fly Ash 1633b.

The investigation was carried out at the University of the Western Cape, SA, and Frank Laboratory of Neutron Physics.

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## INTRODUCTION

Coal fly ash (CFA) is the major waste generated from coal combustion in thermal power station to produce electricity. Worldwide huge amounts of CFA are generated in order to meet energy demands, and about 70 % of CFA is disposed as waste [1]. CFA disposal is of great concern globally due to the environmental issues arising from the disposal methods that are currently employed [2-4]. CFA is considered a highly contaminating medium because the toxic trace elements in coal are accumulated in higher concentrations in the combustion by product [5]. Thus, various environmental risks may be linked to the disposal of CFA in air, soil, surface- and groundwater [6-8].

CFA has been studied extensively to understand the environmental impacts associated with its disposal, management and reuse [6, 9-13]. Research of CFA compositions has shown that the chemical composition of fly ash comprises major (>1wt %), minor (1-0.1wt %), and trace (< 0.1wt %) elements [14]. Elemental analysis has also revealed that rare-earth elements (REEs) (15, 16), toxic elements [17, 18], and radionuclides [19] are present in CFA.

The analytical methods widely used in determining the elemental compositions of CFA are X-ray fluorescence (XRF) spectroscopy [9, 20]; inductively coupled plasma-optical emission spectrometry/mass spectrometry (ICP-OES/MS) [18, 19]; laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) [21] and instrumental neutron activation analysis (INAA) [15, 22].

In South Africa millions of tons of CFA are generated annually by coal-fired power plants in order to meet the large demand for industrial and domestic energy, and the disposal methods currently employed are raising a lot of environmental issues [23, 24]. In the management of CFA, the focus should not only be on the prevention of environmental pollution, but also on methods that can be used to produce or manufacture value-added products from disposed fly ash. In order to achieve these objectives, an accurate method of determining the chemical composition of CFA is fundamental in the qualitative and quantitative analysis of the elements of toxicity and value in fly ash. Instrumental epithermal

neutron activation analysis (ENAA), XRF, ICP-OES and LA ICP-MS were used to determine the elemental composition of CFA. The results obtained will be used in understanding the method that is best suited for determining the different categories of elements that are contained in CFA. This knowledge will assist in the effective valorization and management of CFA.

## MATERIALS AND METHODS

**Sampling.** The CFA samples used in this study were collected directly from the hoppers of Matla coal power station in the Mpumalanga province in South Africa. The fresh CFA samples were put in sealed plastic bags devoid of air to avoid external contamination. The sealed plastic bags were labelled accordingly and stored in a dark, cool cupboard away from any heat source, direct sunlight or fluctuating temperatures.

**Experimental procedures.** *Epithermal Neutron Activation Analysis.* The analysis was carried out at the reactor IBR-2 in Frank Laboratory of Neutron Physics (FLNP), Joint Institute for Nuclear Research (JINR), Dubna. For short irradiation, 100 mg of the CFA sample were heat-sealed in polyethylene bags. For long irradiation, the same amount of the CFA were packed in aluminium cups. To determine short-lived isotopes, the CFA samples were irradiated for 60 s. After irradiation, two gamma-spectrometric measurements were performed; the first one for 3 min after 2–3 min of decay, and the second one for 15 min after 9–10 min of decay. Long-lived isotopes were determined after irradiation for 100 h in the cadmium-screened channel 1. After irradiation samples were repacked into clean containers and measured after 4–5 and 20–23 days for 30 min and for 1.5 h, respectively. Gamma spectra were registered as described elsewhere [25]. The elemental content of a NIST Standard Reference Material 1633 b was also determined by ENAA. The results obtained were then compared to the certified values [26].

*Inductively Coupled Plasma-Optical Emission Spectroscopy.* The digestant for total acid digestion of the selected solid CFA sample included hydrofluoric acid (HF) and aqua regia (HCl and HNO<sub>3</sub> mixed in the ratio of 3:1, respectively). The digestion was carried out according to [27]. 0.25 g of the Matla CFA sample were weighed into a teflon cup; 2 cm<sup>3</sup> of concentrated HF and 5 cm<sup>3</sup> of aqua regia were added. The teflon cup was put in a digestion vessel (Parr bomb), sealed and heated to 200°C for 2 hours in an oven. The Parr bomb was removed from the oven and allowed to cool down. 25 cm<sup>3</sup> of H<sub>3</sub>BO<sub>3</sub> were added to the sample in order to prevent the formation of sparingly soluble species in the sample. The digestant was filtered through 0.45 μm membrane filter and made up to 100 cm<sup>3</sup> with ultrapure water (ELGA Pure lab UHQ). The procedure was triplicated.

The solution obtained from the total acid digestion experiments was analyzed for major and trace concentration using Varian 710-ES ICP optical emission spectrometry. The sample was introduced through a high-sensitivity glass, single-pass cyclone spray chamber and conical nebulizer using argon gas. It was then passed through axially oriented plasma. The wavelength released by different analytes was detected with a CCD detector and autointegrated using ICP Expert II software. The ICP-OES instrument was calibrated before analysis with three calibration standards and a blank (2 % HNO<sub>3</sub>). The certified standards used in calibrating and checking the accuracy of the instrument were supplied by Industrial Analytics. The certified standards were Spectrascan SS-1256 for Si, SS-1206 for Ca, SS1242 for Na, SS-9415S for multiple elements, and SS-028321 for REEs. Three replicates were run for each sample in order to check the reproducibility of the analysis.

*X-Ray Fluorescence Spectroscopy.* CFA samples were crushed into a fine powder (particle size < 100 μm) with a jaw crusher and milled in a tungsten zirconium mill (to prevent contamination from trace and REE) prior to the preparation of a fused disc for major element and trace analysis. The jaw crusher and mill were cleaned with uncontaminated quartz after analyzing each sample to avoid cross contamination. Pressed powder pellets were prepared for XRF analysis using 8 g of the sample and a few drops of MOVIOL (a brand of polyvinylalcohol) was added for binding. The composition was then determined by XRF spectrometry on a Philips 1404 Wavelength Dispersive spectrometer. The spectrometer was fitted with an Rh tube and with the following analyzing crystals: LIF200, LIF220, LIF420, PE, TLAP, and PX1. The instrument is fitted with a gas-flow proportional counter and a scintillation detector. The gas-flow proportional counter uses 90 % argon and 10 % methane gas mixture. Trace elements were analyzed on a pressed powder pellet at various kV and mA tube operating conditions, depending on the analyzed element. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ Philips software. Control standards that were used in the calibration procedures were NIM-G (Granite from the Council for Mineral Technology, South Africa) and BHVO-1 (Basalt from the United States Geological Survey, Reston). The XRF technique reports concentration as % oxides for major elements and ppm (mg/kg) for minor and trace elements. The elements reported as mass % oxides were converted to ppm of the elements using element conversion software downloaded at [28].

*Laser Ablation Inductively Coupled Plasma-Mass Spectrometry.* The instrument was set by connecting a 213 nm laser ablation system connected to an Agilent 7500ce ICP-MS. The CFA sample was coarsely crushed and fusion disks were made by an automatic Claisse M4 Gas Fusion instrument and ultrapure Claisse Flux. A chip of sample was mounted in a 2.4 cm round resin disk. The mounted sample was then polished for analysis. The sample was ablated using He

gas and then mixed with Ar after coming out of the ablation cell. The sample was then passed through a mixing chamber before being introduced into the ICP-MS. Trace elements were quantified using NIST standard 612 for calibration method and  $^{29}\text{Si}$  as internal standard. Three replicate measurements were made on each sample. The calibration standard was run after every 12 samples. A quality control standard was run in the beginning of the sequence as well as with the calibration standards throughout. Both basalt glasses, BCR-2 or BHVO-2G, were certified reference standards produced by USGS (Dr. Steve Wilson, Denver, CO 80225) that were used for this purpose. A fusion control standard from certified basaltic reference material (BCR-2, also from USGS) was also analyzed in the beginning of a sequence to verify ablation on fused material. Data was processed using Glitter software.

## RESULTS AND DISCUSSION

The results obtained on the elemental content in Matla CFA using ENAA, ICP-OES, LA ICP-MS, and XRF are presented below. A total of 54 elements were determined and are summarized in three tables.

To demonstrate the accuracy and reliability of ENAA as the most powerful primary analytical technique [29], NIST Standard Reference Material 1633b (bituminous coal fly ash) was used. The results are given in Tables 1 and 2, subdivided according to the level of certification (certified and noncertified values).

The major elements in fly ash with concentrations  $> 1$  wt. % are presented in Table 3, whilst the minor (1–0.1 wt. %), and trace ( $< 0.1$  wt. %) elements [14] are presented with the REEs in Table 4 and the other trace elements in Table 5. The techniques and principles on which these analytical methods are based are different and each of these techniques has its own merits and demerits which may affect the outcome of the CFA analysis. The composition of the elements in the Matla CFA sample shows that it is Class F since the sum of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  is greater than 70 % [30, 31]. Class F is produced from the burning of bituminous coal and anthracites. Thus, the elemental composition of the Matla CFA can be compared to the given concentrations of the elements in NIST SRM 1633b (bituminous).

**Quality Assurance of ENAA.** To assure the quality of ENAA, the NIST Standard Reference Material 1633b was used. The concentrations of the elements in the NIST SRM 1633b determined by ENAA in Dubna (present value) are compared to the known concentrations of the NIST SRM 1633b (certified value).

It can be seen from Table 1 that there is a strong agreement between the results obtained by ENAA of the NIST SRM 1633b and the certified values of this standard. Except Cu (36.26 %), the RSD % values of the analyzed certified

SRM were below  $\pm 10\%$ . The RSD is used to test for the accuracy of the instrument in order to determine the reliability of the instrument in the analysis of each element. The acceptable range for RSD value is about  $\pm 10\%$ . The RSD % was calculated as follows:

$$\frac{\text{Expected value} - \text{Analytical value}}{\text{Expected value}} \cdot 100\%$$

Expected value is the value of the certified standard; Analytical value is the value obtained when certified standard was analyzed.

**Table 1. Elemental concentrations in the NIST SRM 1633b determined by ENAA in Dubna and the certified values [26]**

Element	NIST certified value, mg/kg	ENAA present value, mg/kg	Minimum detection limit, mg/kg	RSD, %
Al	150500	151000	179	-0.33
As	136.2	133	0.507	2.35
Ba	709	708	21.4	0.14
Ca	15100	15100	691	0.00
Cr	198.2	198	33.3	0.10
Cu	112.8	71.9	662	36.26
Fe	77800	77700	518	0.13
K	19500	20400	4910	-4.62
Mg	4820	4810	176	0.21
Mn	131.8	132	2.8	-0.15
Na	2010	2090	38.5	-3.98
Ni	120.6	121	23.4	-0.33
Se	10.26	9.83	1.39	4.19
Si	230200	230000	334000	0.09
Sr	1041	1040	32.4	0.10
Th	25.7	27.4	0.108	-6.61
U	8.79	8.49	0.286	3.41
V	295.7	312	14.4	-5.51

In Table 2, the noncertified values of some elements in the NIST SRM 1633b are compared to the amounts determined by ENAA in Dubna. Except for Gd(-109.23 %) and Zn(-107.62 %), there is a good agreement between the two values. The RSD % of the analysis is also below  $\pm 10\%$ , however the RSD % values Gd(-109.23 %) and Zn(-107.62 %) clearly show that their determined amounts in the NIST SRM 1633b are inaccurate and unreliable.

**Table 2. Elemental concentrations in the NIST SRM 1633b (noncertified values [26]) and those determined by ENAA in Dubna**

Element	NIST noncertified value, mg/kg	ENAA present value, mg/kg	Minimum detection limit, mg/kg	RSD, %
Br	2.9	2.72	0.454	6.21
Ce	190	190	8.16	0.00
Co	50	47.7	0.326	4.60
Cs	11	11	0.17	0.00
Dy	17	16.2	4.85	4.71
Eu	4.1	4.1	0.776	0.00
Gd	13	27.2	0.718	-109.23
Hf	6.8	8	0.414	-17.65
La	94	92.3	1.43	1.81
Nd	85	157	36.6	-84.71
Rb	140	140	1.84	0.00
Sb	6	5.26	0.0519	12.33
Sc	41	41	0.198	0.00
Sm	20	20	0.0907	0.00
Ta	1.8	1.84	0.038	-2.22
Tb	2.6	2.6	0.0651	0.00
Ti	7910	7920	1760	-0.13
Tm	2.1	1.98	0.353	5.71
Yb	7.6	7.61	1.03	-0.13
Zn	210	436	9.27	-107.62

**Table 3. Concentrations of major elements in Matla CFA determined by ENAA, ICP-OES, and XRF (number of determinations is 3)**

Element	ENAA, mg/kg	ICP-OES, mg/kg	XRF, mg/kg
Si	176000 ± 11314	176760 ± 0.981	225683 ± 0.044
Al	129500 ± 707	62040.13 ± 0.413	163495 ± 0.22
Fe	33100 ± 1453	9201.59 ± 0.074	19661 ± 0.027
Ca	38233 ± 493	17211.72 ± 0.048	47983 ± 0.083
Mg	29233 ± 503	896.19 ± 0.023	12807 ± 0.04
Na	25376 ± 93	21032.51 ± 0.858	4101 ± 0.009
K	6640 ± 464	116.3956 ± 0.008	6985 ± 0.009
P	ND	2539.08 ± 0.025	3873 ± 0.013
Ti	9383 ± 500	9558.16 ± 0.066	7553 ± 0.016
Mn	290 ± 10	132.412 ± 0.002	155 ± 0.0004
S	1420 ± 473	ND*	77.58 ± 0.0024

ND is not detected



Table 3 presents the concentrations of major elements in the Matla CFA determined by ICP-OES, XRF, and ENAA. The major elements were not determined by the LA ICP-MS technique due to unavailability of suitable standards. The results reveal that the major elements analyzed in the Matla CFA were Si, Al, Fe, Ca, Mg, Na, K, P, Ti, Mn, and S. The ENAA technique did not report the concentration of P. From Table 3, the concentration value of the major elements in the Matla CFA obtained using XRF and ENAA were in better agreement when compared to the certified SRM (1633b-NIST) in Table 1. Also, from Table 3 it is observed that the concentrations of the major elements (Al, Fe, Mg, and K) in the Matla CFA obtained using ICP-OES were more than an order of magnitude lower than the concentrations obtained using XRF and ENAA, whereas XRF results of Na were two orders of magnitude lower than ICP-OES and ENAA. However the elemental abundances of these elements seemed to be proportional. The lower concentrations determined by ICP-OES might be attributed to the sample preparation involved in the technique or matrix effects. The ICP-OES/MS is mostly used in determining the concentration of elements in CFA. However, its main disadvantage is that the CFA has to be digested before analysis [32-34]. An acid digestion of fly ash required for ICP-OES may result in either loss or contamination of the sample from the acid and the subsequent dilution technique [35-37]. The Matla CFA was digested prior to ICP-OES and that process may have resulted in the lower elemental concentrations detected in the Matla CFA [38].

The trace element composition of the Matla CFA determined by ENAA, ICP-OES, LA ICP-MS, and XRF is presented in Table 4. The ICP-OES and XRF techniques reported 15 trace elements in the analysis of the Matla CFA while 17 and 23 trace elements were reported by the LA ICP-MS and ENAA techniques, respectively. Cd is not determined by XRF analysis. Also, As and Cd were not obtained by LA ICP-MS, while it is impossible to determine Pb by ENAA. However, As, Cd, Pb were obtained by ICP-OES. These elements are of major environmental concern due to their toxicity. The amounts of the trace elements in the Matla CFA obtained using the LA ICP-MS and ENAA were in better agreement in abundance when compared to the certified SRM (1633b-NIST).

In Table 5, the REEs composition of the Matla CFA determined by ENAA, ICP-OES, LA ICP-MS, and XRF are presented. Ten rare-earth elements were determined by ICP-OES, whilst only three rare-earth elements were determined by XRF technique. LA ICP-OES and NAA allowed determination of 16 and 12 rare-earth elements, respectively. Sc, La, and Ce were the only REEs determined by XRF technique due to unavailability of a suitable standard for calibrating the rare-earth elements. Moreover, the XRF cannot compete with other well-established techniques such as INAA and ICP-MS [39]. The concentrations of the REEs in the Matla CFA obtained by ICP-OES were also much lower compared to the REE concentrations obtained when the Matla CFA was analyzed using XRF, LA ICP-OES and ENAA. This lower concentration of REEs may also be

attributed to the sample preparation used for the ICP-OES as it was observed for the major element concentrations. The concentration of the REEs in the Matla fly ash samples obtained by LA ICP-MS and ENAA are proportional to the given

**Table 4. Concentrations of trace elements in Matla CFA determined by ENAA, ICP-OES, LA ICP-MS, and XRF (number of determinations is 3)**

Element	ENAA, mg/kg	ICP-OES, mg/kg	LA ICP-MS, mg/kg	XRF, mg/kg
V	120 ± 6	ND	154.31 ± 3.49	64.91 ± 6.24
Cr	177.33 ± 19.09	76.09 ± 0.009	183.01 ± 2.41	89.36 ± 2.29
Ni	72.27 ± 2.98	169.62 ± 0.024	49.54 ± 1.80	88.97 ± 6.41
Co	25.90 ± 0.1	2.364 ± 0.001	17.30 ± 0.49	16.08 ± 6.89
Zn	250.33 ± 148.38	26.56 ± 0.002	45.25 ± 2.67	64.61 ± 4.41
As	21.97 ± 4.88	64.22 ± 0.011	ND	20.07 ± 2.68
Nb	ND	519.75 ± 0.041	42.97 ± 1.35	51.50 ± 1.80
Se	1.44 ± 0.64	20.12 ± 0.038	ND	ND
Br	0.55 ± 0.05	ND	ND	ND
Rb	46.67 ± 0.92	0.24 ± 3.29E-06	55.46 ± 2.20	72.48 ± 0.89
Sr	1900 ± 34.64	110.22 ± 0.007	2137.02 ± 81.70	3495.55 ± 5.63
Ag	1.05 ± 0.36	NA	ND	ND
Cd	5.56 ± 2.25	0.11 ± 0.00005	ND	ND
In	0.39 ± 0.12	ND	ND	ND
Sb	2.51 ± 1.03	ND	ND	ND
Cs	10.5 ± 0.1	ND	14	ND
Ba	1823 ± 65	ND	2372.11 ± 32.01	2079.31 ± 12.80
Hf	14.53 ± 0.15	ND	8.63 ± 0.57	ND
Ta	3.46 ± 0.02	ND	2.69 ± 0.11	ND
W	9.01 ± 0.19	ND	ND	ND
Cl	73 ± 5.82	ND	ND	ND
Au	0.0083 ± 0.004	ND	ND	ND
Th	50 ± 0.44	ND	35.44 ± 1.53	46.60 ± 3.33
U	12 ± 0	11.43 ± 0.0132	13.38 ± 0.38	63.28 ± 2.43
Cu	ND	44.45 ± 0.0026	61.84 ± 0.96	117.26 ± 3.38
Mo	ND	4.81 ± 0.0001	10.45 ± 0.33	ND
Pb	ND	22.45 ± 0.006	69.00 ± 1.78	100.25 ± 4.02
Zr	ND	258.93 ± 0.022	313.94 ± 19.57	787.73 ± 3.35

ND is not detected

**Table 5. Concentrations of rare-earth elements in Matla CFA determined by ENAA, LA ICP-MS, ICP-OES, and XRF (number of determinations is 3)**

Element	NAA, mg/kg	ICP-OES, mg/kg	LA ICP-MS, mg/kg	XRF, mg/kg
Sc	33.80 ± 0.79	0.83 ± 0.0001	24.94 ± 1.46	NA
Y	ND	ND	52.3 ± 3.47	103.71 ± 1.46
La	92.23 ± 29.88	0.196 ±	81.66 ± 4.31	111.45 ± 6.51
Ce	247.33 ± 6.66	20.31 ± 0.004	189.78 ± 4.13	226.02 ± 30.00
Sm	18 ± 0	3.72 ± 0.003	11.93 ± 0.56	ND
Eu	3.11 ± 0.12	1.238 ± 0.0006	2.35 ± 0.13	ND
Gd	27.57 ± 0.45	1.163 ± 0.001	10.40 ± 0.82	ND
Tb	2.26 ± 0.19	ND	1.60 ± 0.12	ND
Dy	35.23 ± 1.77	0.44 ± 0.001	9.5 ± 0.56	ND
Tm	1.89 ± 0.72	ND	0.77 ± 0.06	ND
Yb	7.64 ± 1.96	ND	5.27 ± 0.47	ND
Lu	1.26 ± 0.51	0.3 ± 0.0002	0.72 ± 0.042	ND
Nd	88.40 ± 5016	ND	63.50 ± 1.78	ND
Pr	ND	9.53 ± 0.004	18.35 ± 0.60	100.32 ± 2.45
Ho	ND	ND	1.97 ± 0.19	ND
Er	ND	4.3 ± 0.004	5.38 ± 0.28	ND

ND is not detected

concentrations of REEs in the SRM. Hence, LA ICP-MS and ENAA may be considered as better techniques than ICP-OES or XRF analysis in determining the REE concentrations in coal fly ash.

## CONCLUSIONS

For the first time a total of 54 elements, among them 16 rare earths, were determined in the Matla CFA using ENAA, ICP-OES, LA ICP-MS, and XRF techniques. The concentration level of the major elements in the CFA determined by ENAA and XRF is very similar apart from Na and correlates well with that of the certified NIST SRM 1633b. Determination of trace and REEs content obtained by the ENAA and LA ICP-MS techniques is more reliable than their determination by the XRF or ICP-OES techniques. CFA can be considered as a potential source for extraction of rare-earth elements for industrial use. The hazardous impact of heavy metals such as Cd, Pb, As, Sr, U, Th, in particular, observed in the studied CFA should be monitored in the reuse of fly ash in agriculture and construction materials.

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